

PATENT SPECIFICATION

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- (21) Application No. 26273/67 (22) Filed 7 June 1967
(21) Application No. 39232/67 (22) Filed 25 Aug. 1967
(23) Complete Specification filed 4 June 1968
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45Y 606 618 630 771 B4A1 B4H NW
A2B 6A
(72) Inventor JEAN PAUL MARION



(54) FLAVOURING AGENT

- (71) We, NESTLE'S PRODUCTS LIMITED, of Nassau, Bahama Islands, a Company incorporated in the Bahama Islands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 1,2 - diamino propane. The reaction is usually completed within 4—5 hours, yielding 2,3,5 - trimethyl - 5,6 - dihydro pyrazine.
- Dehydrogenation of the dihydrointermediate may be carried out by conventional dehydrogenation techniques, for example by heating the compound with a basic substance such as sodium or potassium hydroxide. This reaction is preferably carried out under an

ERRATA

SPECIFICATION No. 1,220,816

Page 1, Heading, delete "(23) (second occurrence) Complete Specification filed 5 June 1968 45Y 606 618 630 771 B4A1 B4H NW A2B 6A"

Page 1, Heading, after "(52) Index at acceptance" insert "C2C 1G5A 1G5B 1G6A1, 1G6A3 20Y 30Y 321 32Y 455 45Y 606 618 630 771 84A1 B4H NW A2B 6A"

THE PATENT OFFICE
March 1st 1971

- completion of — removed and the 2 - ethyl - 5,5,6 - trimethyl pyrazine recovered by distillation under reduced pressure. It is a colourless liquid with a strong odour resembling roasted vegetable matter.
- The 2,3,5 - trimethyl pyrazine used as a starting material may be prepared by any desired method. In accordance with the present invention, this compound may advantageously be synthesised from butane - 2,3 - dione and 1,2 - diamino propane with subsequent dehydrogenation of the heterocyclic intermediate to obtain the desired pyrazine ring structure. The first stage of this reaction may be carried out at ambient temperatures, preferably in a solvent medium such as ether, substantially equimolar quantities of reactants being employed. Thus, for example, the butane - 2,3 - dione may be added with efficient stirring to an ethereal solution of
- the corresponding dihydro pyrazine is detected in the reaction mixture, a dehydrogenation reaction may be carried out, for example by heating with a basic substance such as potassium hydroxide.
- The 2,3 - diamine butane used as starting material may for example be prepared by reduction of dimethyl glyoxime, for example with Raney nickel and hydrogen or with lithium aluminium hydride.
- (b) Reaction of 2,3 - diamino pentane or a salt thereof with butane - 2,3 - dione
- This reaction may be carried out under conditions similar to those described under (a) above. The 2,3 - diamino pentane used as starting material may be prepared by reduction of methyl ethyl glyoxime, the latter compound being prepared for example, by

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(54) FLAVOURING AGENT

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The present invention is concerned with a pyrazine derivative having useful properties as a flavour enhancer.

It has been found that the compound 2 - ethyl - 3,5,6 - trimethyl pyrazine, hereinafter referred to as ETMP, is an important component of the aroma of cocoa, and it is an object of the present invention to provide methods of synthesising said compound.

In accordance with one preferred embodiment of the invention, 2 - ethyl - 3,5,6 - trimethyl pyrazine is prepared by reacting 2,3,5 - trimethyl pyrazine with ethyl lithium.

Preferably the reaction is carried out below ambient temperatures, for example in the range 0 to -10°C, advantageously in an inert solvent medium such as ether. Upon completion of the reaction, the solvent may be removed and the 2 - ethyl - 3,5,6 - trimethyl pyrazine recovered by distillation under reduced pressure. It is a colourless liquid with a strong odour resembling roasted vegetable matter.

The 2,3,5 - trimethyl pyrazine used as a starting material may be prepared by any desired method. In accordance with the present invention, this compound may advantageously be synthesised from butane - 2,3 - dione and 1,2 - diamino propane with subsequent dehydrogenation of the heterocyclic intermediate to obtain the desired pyrazine ring structure. The first stage of this reaction may be carried out at ambient temperatures, preferably in a solvent medium such as ether, substantially equimolar quantities of reactants being employed. Thus, for example, the butane - 2,3 - dione may be added with efficient stirring to an ethereal solution of

1,2 - diamino propane. The reaction is usually completed within 4—5 hours, yielding 2,3,5 - trimethyl - 5,6 - dihydro pyrazine.

Dehydrogenation of the dihydrointermediate may be carried out by conventional dehydrogenation techniques, for example by heating the compound with a basic substance such as sodium or potassium hydroxide. This reaction is preferably carried out under an inert atmosphere, and upon its completion the 2,3,5 - trimethyl pyrazine may be recovered from the reaction medium as desired, for example by distillation under reduced pressure. It is a colourless liquid with a strong pyrazine odour.

According to the present invention ETMP may also be prepared by any one of the following processes.

(a) Reaction of 2,3 - diamino butane or a salt thereof with pentane - 2,3 - dione

This reaction may be carried out by mixing substantially equimolar proportions of the reactants with stirring, and allowing the mixture to react, for example overnight. The ETMP may be recovered by distillation under conditions similar to those described above. If the corresponding dihydro pyrazine is detected in the reaction mixture, a dehydrogenation reaction may be carried out, for example by heating with a basic substance such as potassium hydroxide.

The 2,3 - diamine butane used as starting material may for example be prepared by reduction of dimethyl glyoxime, for example with Raney nickel and hydrogen or with lithium aluminium hydride.

(b) Reaction of 2,3 - diamino pentane or a salt thereof with butane - 2,3 - dione

This reaction may be carried out under conditions similar to those described under (a) above. The 2,3 - diamino pentane used as starting material may be prepared by reduction of methyl ethyl glyoxime, the latter compound being prepared for example, by

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reaction of pentane - 2,3 - dione with hydroxylamine.

(c) Reaction of an ethyl dimethyl pyrazine with methyl lithium

- 5 Any one of the three isomers of ethyl dimethyl pyrazine (2 - ethyl - 3,5 - dimethyl, 2 - ethyl - 5,6 - dimethyl, 2 - ethyl - 3,6 - dimethyl) may be used as starting material, either singly or as a mixture containing any
- 10 two or all three isomers. The reaction of the pyrazine with methyl lithium is preferably carried out in a solvent such as ether, using substantially equimolar proportions of the reactants. The ETMP may then be recovered
- 15 from the reaction medium by distillation.

The ethyl dimethyl pyrazine starting material may be prepared by any of the following methods:—

- 20 1. Ring halogenation of a dimethyl pyrazine and ethylation of the halogenated compound.

2. Side-chain halogenation of trimethyl pyrazine and methylation of the resulting halogeno-methyl compound.

- 25 3. Methylation of a mono-sodium trimethyl pyrazine.

4. Ring ethylation of dimethyl pyrazine with ethyl lithium or ethyl bromide.

- 30 The conditions under which the above reactions may be carried out are similar to those described herein in connection with the preparation of ETMP or other alkyl pyrazines.

(d) Reaction of trimethyl pyrazine with ethyl bromide

- 35 This reaction is preferably effected in the presence of aluminium chloride as catalyst. The reactants may for example be heated under reflux, in a solvent medium such as carbon disulphide. Small quantities of di-
- 40 methyl diethyl pyrazine and tetramethyl pyrazine may also be formed, and the ETMP is recovered from the reaction mixture by fractional distillation or by fractional crystallisation of a salt.

- 45 (e) Reaction of monosodium tetramethyl pyrazine with a methyl halide.

- This reaction is preferably effected in a solvent medium, advantageously using methyl bromide as the halide. The sodium derivative of tetramethyl pyrazine may be prepared by
- 50 reacting tetramethyl pyrazine with sodamide or with benzyl sodium.

- When sodamide is used, a solution of this reactant may first be prepared by dissolving
- 55 sodium in liquid ammonia and then adding the tetramethyl pyrazine to form the sodium derivative.

(f) Reaction of 2 - halogenomethyl - 3,5,6 - trimethyl pyrazine with a methylating agent.

This reaction is preferably carried out by first forming a Grignard intermediate of the halogeno - methyl - trimethyl pyrazine which is then reacted with a methylating agent such as methyl iodide or dimethyl sulphate. When 2 - bromomethyl - 3,5,6 - trimethyl pyrazine is used as starting material, this substance may for example be prepared by reacting tetramethyl pyrazine with N - bromo - succinimide.

(g) Ethylation of a 2 - halogeno - 3,5,6 - trimethyl pyrazine

The preferred starting material is 2 - chloro - 3,5,6 - trimethyl pyrazine. A Grignard derivative of this compound may first be prepared by reaction with magnesium, and the resulting derivative is then ethylated with an ethylating agent such as diethyl sulphate. The halogeno-trimethyl pyrazine may advantageously be prepared by the method of C. F. Koelsch and W. H. Gumprecht (J. Org. Chem. 23, 1603 (1958)). This method comprises the reaction of trimethyl pyrazine with hydrogen peroxide to yield trimethyl pyrazine N - oxide which is then reacted with a phosphorus oxyhalide.

ETMP may also be formed in small quantities by a reaction between ribose and ammonia or certain amino acids such as α - amino butyric acid, lysine or threonine. ETMP has been detected in roasted coffee and is probably also formed on roasting in other materials containing sugars and amino acids.

The present invention, furthermore, provides a composition for imparting a cocoa flavour to foodstuffs and beverages which comprises 2 - ethyl - 3,5,6 - trimethyl pyrazine.

2 - ethyl - 3,5,6 - trimethyl pyrazine may be added to different cocoa-containing products to enhance the cocoa note. Examples of such products are cocoa mixes, drinking chocolates, chocolate articles of various forms such as bars, filled bonbons, chocolate coatings e.g. for biscuits, confectionery and bakery products, chocolate pudding mixes and the like. Very satisfactory results are obtained by adding 1 to 10 parts by weight of 2 - ethyl - 3,5,6 - trimethyl pyrazine to 100,000 parts by weight of cocoa solids. Amounts at the lower end of the range (1—5 parts/10⁵) are preferred for products containing a high proportion of cocoa, for example dark (plain) chocolate, whereas higher quantities (5—10 parts/10⁵) may be added to products containing less cocoa, such as milk chocolate or beverage mixes. The compound may also be incorporated in a synthetic cocoa flavour.

The following Examples are given only for the purposes of illustrating the invention. All parts are parts by weight.

EXAMPLE 1

a) Preparation of 2,3,5 - trimethyl pyrazine

116 g (1.35 mole) of butane - 2,3 - dione are added dropwise to 100 g (1.36 mole) of 1,2 - diamino propane in 200 ml of diethyl ether. The resulting thick white solution becomes clear and yellow after 4—5 hours' vigorous stirring. The ether is removed, leaving 158 of 2,3,5 - trimethyl - 5,6 - dihydro pyrazine which is then heated for 3 to 5 hours under reflux with about 40 g of potassium hydroxide pellets. This operation is carried out under nitrogen. Finally, the reaction mixture is distilled under reduced pressure (59—63°C, 9 mm Hg) yielding 96 g of 2,3 - trimethyl pyrazine.

Analysis:

Calculated for $C_7H_{11}N_2$: 122.0844, found (mass spectrometry): 122.0841; $n_D^{25} = 1.4970$.

Gas chromatography: retention index (Kovats)=1005, using a 6 m column 0.8 cm in diameter, containing Chromosorb W(45-60 mesh) ("Chromosorb" is a Registered Trade Mark) and 20% of Silicone Gum Rubber; helium feed rate: 150 ml/min, temperature 160°C.

b) Preparation of 2 - ethyl - 3,5,6 - trimethyl pyrazine

A solution of ethyl lithium is prepared from 6 g of lithium and 47 g of ethyl bromide, by the method described by H. Gilman, J. A. Bael, C. G. Brannen et al, J. Am. Chem. Soc 71, 1499 (1949). This solution is cooled to -10°C and 39 g of trimethyl pyrazine are added dropwise. The solution, which turns red in colour and thickens, is stirred for 1.5 hours without refrigeration. It is then cooled again to -10°C and ice water is added up to clarity. The mixture is extracted three times with ether and once with chloroform, the extracts are dried over sodium sulphate and the solvents are evaporated. The residue is distilled at 85—90°C at 10 torr to provide 2 - ethyl - 3,5,6 - trimethyl pyrazine of 95% purity, the remainder consisting principally of tri- and tetra - methyl pyrazine. It may be further purified by redistillation.

Analysis:

Calculated for $C_{10}H_{13}N_2$: 150.1157, found (mass spectrometry): 150.1149; $n_D^{25} = 1.4893$.

Gas chromatography (conditions as above): Retention index (Kovats)=1150.

Infra red spectrum, liquid film (CsBr plates), grating instrument: principal bands at 2966(s), 2943(s), 2878(m), 1655(m), 1454(m), 1415(m), 1372(m), 1205(w), 1172(w).

EXAMPLE 2

(i) Preparation of 2,3 - diamine butane

A mixture of dimethyl glyoxime (11.6 g) and Raney nickel alloy (17.7 g) is added portionwise with stirring and cooling at 10°C to sodium hydroxide solution (5%, 200 ml) and the reaction mixture is left overnight. The diamine may then be extracted with a solvent or, preferably, it is converted into the hydrochloride (cf. F. H. Dickey et al, J. Am. Chem. Soc. 74, 944 (1952)) which is then dried by azeotropic distillation with isopropyl alcohol. It may then be used in the next step of the synthesis without further purification.

Alternatively, dimethyl glyoxime (11.6 g) is reduced with an excess of lithium aluminium hydride (10 g) in ether. The reaction is carried out under reflux with stirring, and the solution is allowed to stand overnight. Dry ethyl acetate is then added and the solution is filtered and concentrated under vacuum to give a concentrated solution of 2,3 - diamino butane in dry ethyl acetate.

(ii) Preparation of ethyl trimethyl pyrazine

Pentane - 2,3 - dione (10 g) in ether (100 ml) is added to a concentrated ethyl acetate solution of 2,3 - diamino butane obtained as described above and the mixture is stirred overnight at room temperature.

Upon completion of the reaction, pure ethyl trimethyl pyrazine is recovered by distillation at 85—90°C under reduced pressure (10 torr). Ethyl trimethyl pyrazine may also be isolated from the reaction mixture by first forming a salt (e.g. the hydrochloride), crystallising the salt and subsequently adding alkali to liberate the base.

Alternatively, the ethyl acetate solution of 2,3 - diamino butane may be replaced by an equivalent quantity of dry 2,3 - diamino butane hydrochloride. The hydrochloride is first suspended in ether and potassium hydroxide (2 g) is added to liberate the diamine.

Before isolating the ethyl trimethyl pyrazine, the reaction mixture may be examined by gas chromatography for the presence of the dihydrocompound (2 - ethyl - 3,5,6 - trimethyl - 5,6 - dihydro pyrazine). If this compound is detected in notable quantities, it may be dehydrogenated by heating the mixture with potassium hydroxide.

EXAMPLE 3

Butane - 2,3 - dione (8.6 g) is added to a solution of 2,3 - diamino pentane (10 g) (prepared by reduction methyl ethyl glyoxime with Raney nickel or $LiAlH_4$) in anhydrous ether (100 ml) and the mixture is allowed to react overnight with stirring and occasional heating. Upon completion of the reaction, the mixture is concentrated and pure ethyl trimethyl pyrazine is recovered by dis-

tillation as described in Example 2, any dihydrocompound present being first dehydrogenated.

EXAMPLE 4

5 (i) Preparation of ethyl dimethyl pyrazines
Pentane - 2,3 - dione (0.2 mol) is added
dropwise to a solution of 1,2 - diamino -
propane (0.2 mol) in anhydrous diethyl ether
10 (200 ml) and the mixture is stirred vigorously
until a clear solution is obtained (3—
5 hours). Thereafter the solvent is removed.
Analysis of the residue by preparative gas-
liquid chromatography indicates the presence
15 of both 3 - ethyl - 2,6 - dimethyl pyrazine
(Kovats retention index=1080) and 3 - ethyl-
2,5 - dimethyl pyrazine (retention index=
1105). A mixture of the corresponding di-
hydro compounds (retention index=1130) is
20 also detected. The reaction products are
warmed for 2 to 3 hours with potassium
hydroxide pellets (5 g) to complete the de-
hydrogenation of the pyrazine ring. The re-
tention indices were obtained using the
25 column and under conditions described in
Example 1.

(ii) Preparation of ethyl trimethyl pyrazine
A mixture of ethyl dimethyl pyrazines pre-
pared as described above is added to a cooled
30 solution of methyl lithium (obtained from
methyl iodide (34 g) and lithium (1.4 g)) in
anhydrous diethyl ether (200 ml) and the
reaction allowed to proceed for several hours.
Thereafter the solvent is removed and ethyl
trimethyl pyrazine is recovered from the resi-
35 due by distillation as described in Example
2.

EXAMPLE 5

Trimethyl pyrazine (5 g) is heated under
reflux with ethyl bromide (5 g) in a solution
40 of carbon disulphide (100 ml), in the presence
of aluminium chloride (11 g) as catalyst. Up-
on completion of the reaction, ice water is
added and the mixture is extracted with
ether (3×50 ml). The solvent is then re-
45 moved and ethyl trimethyl pyrazine is re-
covered from the residue by distillation as
described in Example 2.

EXAMPLE 6

Sodium (0.7 g) is added in small portions
50 to liquid ammonia (200 ml), followed by
tetramethyl pyrazine (4 g), whereupon the
colour changes from blue to red. Thereafter
methyl bromide (6 to 8 g) is bubbled into the
solution).
55 When all the methyl bromide has been
added, the ammonia is replaced by ether (100
ml) and the ethereal solution is dried over
sodium sulphate. The solvent is then re-
moved and ethyltrimethyl pyrazine is re-
60 covered from the residue by distillation as
described in Example 2.

Alternatively, the residual tetramethyl pyra-
zine may be crystallised out of the solution
leaving substantially pure ethyl trimethyl
pyrazine in the mother liquor.

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EXAMPLE 7

i) Preparation of 2 - bromomethyl - 3,5,6-
trimethyl pyrazine

Benzoyl peroxide (0.3 g) is added to a
solution of tetramethyl pyrazine (4.1 g) in
70 anhydrous carbon tetrachloride (150 ml), fol-
lowed by N - bromo - succinimide (5.4 g).
The solution, in a glass flask, is illuminated
by a 500-watt lamp and stirred for 2 hours.
It is then filtered and the filtrate, consisting
75 of 2 - bromomethyl - 3,5,6 - trimethyl pyra-
zine, is concentrated. (Retention index=
1320).

(ii) Preparation of ethyl trimethyl pyrazine
2 - bromomethyl - 3,5,6 - trimethyl pyra-
zine (6.4 g) is added to anhydrous diethyl
ether (100 ml) containing magnesium turn-
ings (0.8 g). Methyl iodide (4.3 g) is then
added to the solution of the resulting Grig-
nard compound and the mixture is allowed to
85 react for 24 hours with stirring.

Thereafter, ice water is added, and the
mixture is extracted with ether, the extract
is dried over sodium sulphate and the sol-
vent is removed. Ethyl trimethyl pyrazine is
90 recovered from the residue by distillation as
described in Example 2. If desired, dimethyl
sulphate may be used as methylating agent
instead of methyl iodide.

EXAMPLE 8

(i) Preparation of 2 - chloro - 3,5,6 - tri-
methyl pyrazine

Hydrogen peroxide (30%, 11.5 g) in solu-
tion in acetic acid (100 ml) is mixed with
trimethyl pyrazine (12.2 g), as described by
100 C. F. Koelsch and W. H. Gumprecht (J.
Org. Chem. 23, 1603 (1958)). Phosphorus
oxychloride (45 ml) is then added to the re-
sulting pyrazine N - oxide, the mixture heated
under reflux for 15 minutes and left to react
105 for 1 hour. Excess POCl₃ is distilled off,
leaving 2 - chloro - 3,5,6 - trimethyl pyra-
zine which may be used directly in the next
step.

(ii) Preparation of ethyl trimethyl pyrazine
2 - chloro - 3,5,6 - trimethyl pyrazine
110 (15 g) is added to fine magnesium turnings
(2.4 g) in tetrahydrofuran (200 ml). Diethyl
sulphate (31 g) is then added to the result-
ing Grignard derivative and the reaction
115 allowed to proceed overnight. Thereafter, ice
water is added, the mixture is extracted with
ether, the extract is dried over sodium sul-
phate and the solvent is removed. Ethyl tri-
methyl pyrazine is recovered from the resi-
120 due by distillation as described in Example
2.

EXAMPLE 9

- 5 ppm of 2 - ethyl - 3,5,6 - trimethyl pyrazine (95% purity) prepared as described in Example 1 are added to 100 parts of a hot beverage containing 3 parts of cocoa solids and 12 parts of sugar. A standard is also prepared omitting the 2 - ethyl - 3,5,6 - trimethyl pyrazine.

- A panel of 10 trained tasters preferred the beverage with added 2 - ethyl - 3,5,6 - trimethyl pyrazine.

EXAMPLE 10

- 2 - ethyl - 3,5,6 - trimethyl pyrazine is added to plain (dark) chocolate (55% cocoa solids) at a level of 2 parts per 100,000 parts of cocoa. The chocolate has a stronger, fuller flavour than a standard without addition of 2 - ethyl 3,5,6 - trimethyl pyrazine.

EXAMPLE 11

- 2 - ethyl - 3,5,6 - trimethyl pyrazine is added to milk chocolate (15% cocoa solids) at a level of 7 parts per 100,000 parts of cocoa. The chocolate has a fuller cocoa note.

EXAMPLE 12

- A mixture of the following substances is prepared:—

	parts
2 - ethyl - 3,5,6 - trimethyl pyrazine	551
Benzaldehyde	11
Furyl methyl ketone	4
Ethyl benzoate	7
2 - phenyl - ethyl acetate	86
Furfuryl alcohol	15
Acetophenone	31
γ - butyrolactone	85
1 - phenyl ethanol	44
2 - phenyl ethanol	166
	<hr/> 1000

- 5 ppm of this composition are added to 100 parts of hot water containing 5 parts of sugar and 0.01 parts of vanillin. The resulting beverage has a pronounced cocoa note.

WHAT WE CLAIM IS:—

1. A process for the preparation of 2 - ethyl 3,5,6 - trimethyl pyrazine in which 2,3,5 - trimethyl pyrazine is reacted with ethyl lithium.
2. A process according to claim 1 in which the reaction is effected at a temperature between 0 and -10°C .
3. A process according to claim 1 or claim 2 in which the reaction is effected in an inert solvent medium.
4. A process according to any one of the preceding claims in which the 2,3,5 - trimethyl pyrazine used as starting material is prepared by reacting butane - 2,3 - dione with

1,2 - diamino propane and dehydrogenating the resulting 2,3,5 - trimethyl - 5,6 - dihydro pyrazine.

5. A process according to claim 4 in which the dehydrogenation is effected by heating 2,3,5 - trimethyl - 5,6 - dihydro pyrazine with a basic substance.

6. A process according to claim 5 in which the basic substance is sodium or potassium hydroxide.

7. A process according to claim 1 substantially as herein described with reference to Example 1.

8. A process for preparing 2 - ethyl - 3,5,6 - trimethyl pyrazine in which 2,3 - diamino butane or a salt thereof is reacted with pentane - 2,3 - dione.

9. A process according to claim 8 in which substantially equimolar proportions of the reactants are used.

10. A process according to claim 8 or claim 9 in which, upon completion of the reaction, the reaction mixture is heated with a basic substance.

11. A process according to any one of claims 8 to 10 in which the 2,3 - diamino butane is prepared by reducing dimethyl glyoxime with Raney nickel and hydrogen or with lithium aluminium hydride.

12. A process according to claim 8, substantially as hereinbefore described with reference to Example 2.

13. A process for preparing 2 - ethyl - 3,5,6 - trimethyl pyrazine in which 2,3 - diamino pentane or a salt thereof is reacted with butane - 2,3 - dione.

14. A process according to claim 13 in which substantially equimolar proportions of the reactants are used.

15. A process according to claim 13 or claim 14 in which the 2,3 - diamino pentane is prepared by reducing methyl ethyl glyoxime.

16. A process according to claim 13 substantially as hereinbefore described with reference to Example 3.

17. A process for preparing 2 - ethyl - 3,5,6 - trimethyl pyrazine in which an ethyl dimethyl pyrazine is reacted with methyl lithium.

18. A process according to claim 17 in which substantially equimolar proportions of the reactants are used.

19. A process according to claim 17 substantially as hereinbefore described with reference to Example 4.

20. A process for preparing 2 - ethyl - 3,5,6 - trimethyl pyrazine in which trimethyl pyrazine is reacted with ethyl bromide.

21. A process according to claim 20 in which the reaction is carried out in the presence of aluminium chloride as catalyst.

22. A process according to claim 20 or claim 21 in which the reaction is carried out in carbon disulphide as solvent medium.

23. A process according to claim 20 substantially as hereinbefore described with reference to Example 5.
24. A process for preparing 2 - ethyl - 3,5,6 - trimethyl pyrazine which comprises reacting monosodium tetramethyl pyrazine with a methyl halide.
25. A process according to claim 24 in which the methyl halide is methyl bromide.
26. A process according to claim 24 or claim 25 in which the monosodium tetramethyl pyrazine is prepared by reacting tetramethyl pyrazine with sodamide or with benzyl sodium.
27. A process according to claim 24 substantially as hereinbefore described with reference to Example 6.
28. A process for preparing 2 - ethyl - 3,5,6 - trimethyl pyrazine which comprises reacting a 2 - halogenomethyl - 3,5,6 - trimethyl pyrazine with a methylating agent.
29. A process according to claim 28 in which the halogenomethyl trimethyl pyrazine is first converted into a Grignard intermediate which is then reacted with a methylating agent.
30. A process according to claim 28 or claim 29 in which the halogenomethyl trimethyl pyrazine is 2 - bromomethyl - 3,5,6 - trimethyl pyrazine.
31. A process as claimed in any one of claims 28 to 30 in which the methylating agent is methyl iodide or dimethyl sulphate.
32. A process according to claim 28 substantially as hereinbefore described with reference to Example 7.
33. A process for preparing 2 - ethyl - 3,5,6 - trimethyl pyrazine which comprises ethylating a 2 - halogeno - 3,5,6 - trimethyl pyrazine.
34. A process according to claim 33 which comprises reacting 2 - chloro - 3,5,6 - trimethyl pyrazine with magnesium and ethylating the resulting Grignard derivative.
35. A process according to claim 33 substantially as hereinbefore described with reference to Example 8.
36. 2 - ethyl - 3,5,6 - trimethyl pyrazine whenever prepared by a process as claimed in any one of claims 1 to 7.
37. 2 - ethyl - 3,5,6 - trimethylpyrazine whenever prepared by a process according to any one of claims 8 to 35.
38. A foodstuff or beverage comprising cocoa and added 2 - ethyl - 3,5,6 - trimethyl pyrazine.
39. A foodstuff or beverage according to claim 38 comprising 1 to 10 parts by weight of added 2 - ethyl - 3,5,6 - trimethyl pyrazine per 100,000 parts by weight of cocoa.
40. Plain (dark) chocolate containing 1 to 5 parts by weight of added 2 - ethyl - 3,5,6 - trimethyl pyrazine per 100,000 parts by weight of cocoa solids.
41. A foodstuff or beverage according to claim 38 substantially as herein described with reference to any one of Examples 9 to 11.
42. A composition for imparting a cocoa flavour to foodstuffs and beverages which comprises 2 - ethyl - 3,5,6 - trimethyl pyrazine.
43. A composition according to claim 42 substantially as herein described with reference to Example 12.
44. A process for flavouring foodstuffs and beverages which comprises incorporating 2 - ethyl - 3,5,6 - trimethyl pyrazine in said foodstuffs or beverages.
45. A process according to claim 44 in which the foodstuff or beverage contains cocoa and 1 to 10 parts by weight of 2 - ethyl - 3,5,6 - trimethyl pyrazine are added per 100,000 parts by weight of cocoa present in the foodstuff or beverage.
46. A process for flavouring plain (dark) chocolate which comprises incorporating from 1 to 5 parts by weight of 2 - ethyl - 3,5,6 - trimethyl pyrazine per 100,000 parts by weight of cocoa solids present in the chocolate.
47. 2 - ethyl - 3,5,6 - trimethyl pyrazine.

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Agents for the Applicants.

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